REVIEW ARTICLE Volume 2, 2018

ISSN Print 2663-0141
ISSN Online 2663-015X

THE INTERNATIONAL JOURNAL OF GLOBAL SCIENCES (TIJOGS)

Synthesis and characterization of nanoparticles for agricultural applications

Ishrat Fatima[1]✉, Muhammad Aslam[2], Muhammad Waqas Yonas[3], Muhammad Haroon[4], Muhammad Saqib Mushtaq[5], Faheem Abbas and Muhammad Usman Tahir[6]

1.Department of Physics, Islamia University Bahawalpur, Pakistan
2.College of Physics and Engineering, Hebei Normal University, China
3.Muhammad Nawaz Sahreef Unievrsity of Agriculture, Multan
4.Huazhong Agriclultural University, Hubei China
5. Department of Plant Pathology, University of Agriculture, Faisalabad
6.Department of Chemistry, University of Agriculture, Faisalabad

✉**Corresponding author:**
Ishrat Fatima
Department of Physics, Islamia University Bahawalpur, Pakistan
Email: fatimaishrat661@gmail.com

Article History
Received: 05 November 2018
Accepted: 22 January 2019
Published: 11 February 2019

How to Cite?
(Fatima *et al., 2019*)
Ishrat Fatima, Muhammad Aslam, Muhammad Waqas Yonas, Muhammad Haroon, Muhammad Saqib Mushtaq, Faheem Abbas and Muhammad Usman Tahir. Synthesis and characterization of nanoparticles for agricultural applications. *The Int. J. Global. Sci*. 2019,2(1),32-37(ISSN2663 -0141(print); ISSN 2663-015X(online).
(http://www.rndjournals.com/)

ABSTRACT

Nanotechnology is an emerging field of science and technology to produce, design, characterize and use structures, systems and devices by controlling size and shape at nanoscale level. Nanotechnology has become an interdisciplinary technology that has connected scientific fields such as chemistry, physics, agriculture, material sciences and medicine. Nanoparticles exhibit improved physical, chemical and biological properties based on specific characteristics such as size distribution and morphology. Due to their size nanoparticles have higher surface to volume ratio having distinct properties as compared to the bulk counterpart offering many new developments in biosensors, nano fertilizers, nano pesticides and many more. Growth and yield of crops can be improved by developing new agrochemicals using nanotechnology. Size and shape of various nanomaterials is an important factor for their agricultural applications. Attempts are being made to develop different nanoparticles for slow release, minimize pollution, increase germination and growth rate with improvement in yield. Metal oxide nanoparticles can be called multi-functional materials due to their unique properties and versatile applications as pesticide, fungicide and fertilizer.

INTRODUCTION

Nanotechnology is an emerging field of science and technology to produce, design, characterize and use structures, systems and devices by controlling size and shape at nanoscale level (Sattler, 2010). Innovations in the field of nanotechnology are due to the extensive research on nanoparticles for the unique properties of nanoproducts compared to the bulk (Sabir *et al.*, 2014). Nanotechnology has become an interdisciplinary technology that has connected scientific fields such as chemistry, physics, agriculture, material sciences and medicine (Shevchenko *et al.*, 2006). Nanoparticles exhibit improved physical, chemical and biological properties based on specific characteristics such as size distribution and morphology. Due to their size nanoparticles have higher surface to volume ratio having distinct properties as compared to the bulk counterpart offering many new developments in biosensors, nano fertilizers, nano pesticides and many more (Nalwa, 1999).

Nanotechnology has produced a variety of materials with one or more dimensions at the nano scale and hence can be classified based on one, two and three dimensions (Hett, 2004). Thin films, a one dimensional system has numerous applications in electronics and engineering including information storage systems, fiber optics and bio-sensors. Carbon nanotubes, a two dimensional system is a hexagonal network of carbon atoms having great capacity for molecular absorption and chemically very stable material (Kohler and Fritzsche, 2008). Quantum dots, a three dimensional system are small devices containing a tiny droplet of free electrons commonly used in vivo imaging, tissue engineering and drug delivery systems (Larson *et al*., 2003).

Metal oxide nanoparticles are of great interest due to their safe, cheap, environment friendly, easy synthesis procedure and technological applications in physics as well as medical and biology. To synthesize nanoparticles of various shapes, size and composition depending on specific requirements, numerous methodologies has been developed such as precursor from liquid, solid or gas phase. Co-precipitation and sol-gel are wet chemical synthesis approaches offering simple and better size control. The synthesis of nano particles by co-precipitation method consists of oxidation by bubbling oxygen gas through an aqueous suspension of hydroxides of metal and other di or trivalent ions by adding an alkaline solution to obtain powders with high homogeneity and purity (Yattinahalli *et al*, 2013). Sol-gel method allows synthesizing nano particles of high purity and better homogeneity compared to the traditional process of oxide fusion. Gas phase synthesis of nano particles is based on nucleation and growth in an inert gas environment and the processing is mainly by laser ablation, electro spray, plasma spray and spray pyrolysis (Saravanan *et al*., 2008). Laser ablation is an attractive method due to its ability to offer narrow size distribution and a low level of impurities. Synthesis parameters such as laser wave length, energy, pulse width and ablation time can affect the characteristics of nano particles (Ganeev, 2010).

The intrinsic properties of metal nanoparticles are mainly determined by size, shape, composition, crystallinity and morphology. Metal oxides play very vital role in many fields of science and technology such as Physics, Chemistry, Material Science and Engineering and Medicines. Metal elements are able to make chemical bond with oxygen and form oxidic compounds. These oxidic compounds can take up large number of structural geometries with an electronic structure that can demonstrate metallic, semiconductor or insulator distinctiveness. In these days, metal oxide nanostructures having unique physical and chemical properties because of their small size, high aspect ratio i.e. surface to volume ratio of atoms and edge effect are widely used in the fabrication of solar cells, sensors, fuel cells, microelectronic circuits, as a catalyst and piezoelectric devices (Wang and Wenzhuo, 2012).

Agriculture has economically much importance in our country but unfortunately agriculture sector is facing many global challenges and environmental issues such as accumulation of pesticides and fertilizers so there is strong need to adopt efficient techniques to make agriculture more sustainable (Chen and Yadha, 2011). Applications of nanotechnology in agricultural production could play an important role particularly to the application of plant protection products, nutrient losses in fertilization and enhance yields by optimized nutrients. Nanoparticles provide an efficient mean to distribute pesticides and fertilizers in a controlled fashion with high efficiency and reducing collateral damage. Metal oxide nano particles especially ZnO have ability to enhance the yield and growth of food crops. Peanut seeds treated with different concentrations of ZnO nano particles (25nm particle size) promoted seed germination and plant growth along with increasing stem and root growth (Prasad *et al*., 2012). The colloidal solution of metal oxides can be used as nano fertilizer because it is a plant nutrient which is more than a fertilizer reviving the soil to an organic state without harmful factors. The yield of wheat plants grown from treated seeds treated with metal nano particles on average increased 20-25% (Batsmanova *et al*., 2013).

The development of nanotechnology devices has recently become one of the most emerging fields of research in the physical sciences. Enhancing the surface area without increasing the device dimension leads to more efficient devices based on surface controlled phenomena such as in solar cells, sensors, detectors, targeted drug delivery and catalysis. Numerous research groups have developed techniques that utilize metal oxide nanostructures to fabricate devices. However, widespread utilization of nanotechnology is often hindered by the conflicting demands for precise control of size, shape, morphology, their physical properties and low-cost mass production. It is therefore necessary to develop and establish a technology that allows for rapid low cost production of high surface area nanostructures with desired properties (Purica *et al*., 2001). Soft chemical routes are; low cost, versatile methods which can be used to synthesize metal oxide nanostructures. Desired properties can be rendered in the metal oxide nanostructures by simple techniques such as chemical doping in the precursor solutions. The objective of this proposed study is to synthesize ZnO nano particles with the most practical and economical ways, to optimize ZnO nanostructures for sustainable agricultural applications.

REVIEW OF LITERATURE

Atomic and molecular properties of elements alter in deriving nano particles having unusual and fascinating properties (Kato, 2011). Materials behave quite differently at nanoscale associated with high surface to volume ratio which increases as the particle size decreases. As the particle size decreases to some degree, the surface of particles found surrounded by large number of atoms which causes high reactivity with prominent physical properties. Nanoparticles of specific materials show unique properties, hence control and manipulation of material properties can be obtained. In past, researchers have been involved in the development of synthetic methods enabling the size and morphological control of nanoparticles. There are different types of nanoparticles, e.g metal, metal oxide and polymer nanoparticles. Due to their diverse properties and functionalities metal oxide nanoparticles are most versatile. ZnO nanoparticles have much importance for their vast area of application, particularly in optical and electronic devices (Aoki *et al*., 2000), biomedical instruments and medicines (Ayudhya *et al*., 2006) and sustainable agriculture (Chen and Yada, 2011). Numerous routes have been used for the synthesis of ZnO nanomaterials, such as sol–gel synthesis (Wang, 2004), hydrothermal methods (Teja and Koh, 2009), microemulsion method co-precipitation and physical vapor deposition.

Synthesis of ZnO nanoparticles was carried out by simple precipitation method using zinc sulfate and sodium hydroxide and calcined for 2 hr at different temperatures. Highly pure Nano scale particles were observed using EDS and Debye-Scherrer's formula respectively with various morphological changes confirmed by SEM images (Reddy *et al*., 2012). The morphology of the nanoparticles can be changed by changing the solvents (Khorsand *et al.,* 2011). The effect on morphology of ZnO by acidic and basic solution routes was observed by preparing ZnO nanoparticles having different aspect ratios. ZnO rods and grains were obtained in a synthetic process having various aspect ratios in a 2hr reaction at 60°C via an acidic route in aqueous solution of $ZnSO_4$ with addition of NaOH and via a basic route in a basic solution of NaOH with addition of $ZnSO_4$ with the same final pH. Characterization via XRD showed peak broadening in acidic route as compared to the basic route confirming that acidic route forms smaller particles. Formation of ZnO particles via acidic route and ZnO rods via basic route was confirmed by FESEM images. Spherical shaped particles with diameters of 32nm and ellipsoidal with a diameter of 44nm were obtained via the acidic route. Due to the low solubility of ZnO the degree of saturation was extremely high at the initial stage of the acidic route producing much higher number of ZnO nuclei via the acidic route having the same final pH value and $[OH^-]/[Zn^{2+}]$ while in the basic route ZnO nanorods were formed due to inadequacy of formed ZnO nuclei at the initial stage increased particle size was observed via subsequent growth in progressive stage (Kawano and Imai, 2006).

Using solvothermal method the effect of solvent on the morphology of crystalline ZnO nanoparticles was investigated using SEM, TEM and XRD. As a precursor zinc acetate suspended in alcohols, glycols, alkanes and aromatic solvents was used for a 2hr reaction time and heated between 250–300°C (Ayudhya *et al*., 2006). ZnO particles were deposited via the chemical deposition method over Al_2O_3 plate performing hydrolysis based reactions of zinc acetate in methanol solvent for 24 hr at 60°C to investigate the morphological evolution by the addition of water in the precursor-methanol solution. The shape and size of ZnO particles changed by increasing water/methanol volume ratio. The shape changed from irregular particles to plates and then from plates to regular cones of height inversely related to the volume of added water and size change from nanoscale to micro-scale. By adjusting the volume ratio shape and size of ZnO can be controlled (Wang *et al*., 2005). Control of the size ranging 25–100 nm with almost uniform and spherical morphologies of ZnO was attained by ester-fication of zinc acetate and ethanol adjusting reaction temperature 100-200°C for a time of 24-48 hr. High crystallinity and uniform sphericity of ZnO nanoparticles was confirmed by XRD and TEM analysis concluding that nanoparticle size coulde asily be controlled by changing the reaction time and temperature (Du *et al*., 2004).

Low temperature solution approach from a single molecular precursor for ZnO nanoparticles without using any base, surfactant or template was adopted. As a precursor zinc acetate dihydrate was used and methanol as a solvent at 60°C for 10 hr. To check the effect of the solvent polarity and water miscibility on the growth of ZnO nanoparticles a mixture solvent i.e., dimethylformamide (DMF), toluene, and THF with methanol was used. Controlled growth rate with pure ZnO nanoparticles was achieved using a non-polar water-immiscible solvent and fully defected particles were generated using the water-miscible polar solvent (Uthirakumar *et al*., 2007). Control over shape and size of ZnO nanoparticles was gained using simple polyol synthetic method. The method and amount of added water determined the size and characteristics of nanoparticles. Water can stimulate hydrolysis and condensation reactions of the Zn when injected into a hot Zn precursor solution at 180°C to induce homogenous nucleation leading the growth of aggregated equiaxial ZnO nanoparticles having average diameter of 24 nm. By increasing the amount of water in the precursor solution increases the particle size and enlarges aspect ratio of rod-shaped particles. Particles size and aspect ratio was slightly influenced by zinc acetate concentration. Increasing hydration ratio particle diameter increased from 24 to 32 nm showing a slight deviation from equiaxial growth (Lee *et al*., 2008).

Sol-gel method gives homogenous, high-purity, and high-quality nanopowders. To synthesis ZnO colloidal spheres through two types of reaction processes were used, one by adding 0.01 M zinc acetate dihydrate to 100 ml diethylene glycol (DEG) and heated at 160°C for 1 hr andother by adding 0.01 M zinc acetate and 5–20 ml of primary supernatant to produce 50–300 nm white colloidal ZnO depending upon the amount of primary supernatant. Analytical techniques including XRD, TEM, Raman spectroscopy, and UV photoluminescence measurement were used to check the structural and optical properties confirming hexagonal wurtzite crystallites, spherical clusters of 185 nm-diameter, crystallinity and defect-bound excitons of ZnO nanoparticles (Lin *et al., 2005*).

Multifunctional inorganic Zinc oxide nanoparticles were fabricated using grapefruit (Citrus paradisi) peel extract having particle size ranging from 12 to 72 nm. UV-Vis spectrophotometer, TEM, DLS, and FTIR analysis were used for characterizing structural, morphological, and optical properties and concluded that green ZnO nanoparticles could be used effectively in medical and environmental safety applications (Kumar *et al.,* 2014). Exploring beneficial uses of nanoparticles in plant sciences is becoming an increasingly important area of interest (Rycenga *et al.,* 2011). Nowadays mechanisms and effects of nanomaterials on plant growth are being studied with high-tech instruments and modern techniques. Improvement in growth and yield of crops in the field of agriculture can be obtained using nanoparticles. Seedling growth, germination rate and yield of wheat were tested by applying silver nanoparticles prepared by chemical route and found that it increased leaf area, number of seminal roots, root biomass, fresh and dry weight having no effect on germination when applied at the rate of 25-50 ppm. Maximum number of grains per spike was observed at 25 ppm and 50 ppm with maximum grain weight as weighed 100 grains was found at 25 ppm and 125 ppm (Razzaq *et al.,* 2015).

ACKNOWLEDGEMENT: All authors contributed equally in collecting and writing a review

CONFLICT OF INTEREST : Nothing to declare

REFERENCES

1. Aoki, T., Y. Hatanaka and D.C. Look. 2000. ZnO diode fabricated by excimer-laser doping. Appl. Phys. Lett. 76: 3257-3258.
2. Ayudhya, S.K.N., P. Tonto, O. Mekasuwandumrong, V. Pavarajarn and P. Praserthdam. 2006. Solvothermal synthesis of ZnO with various aspect ratios using organic solvents. Cryst. Growth Des. 6: 24-46.
3. Batsmanova, L., L. Gonchar, N.Y. Taran and A. Okanenko. 2013. Using a colloidal solution of metal nanoparticles as micronutrient fertiliser for cereals.

Proceedings of the international conference nanomaterials: applications and properties. 2: 2-5.
4. Chen, H. and R. Yada. 2011. Nanotechnologies in agriculture: New tools for sustainable development. Trends Food Sci. Technol. 22: 585-594.
5. Du, H., F. Yuan, S. Huang, J. Li and Y. Zhu. 2004. A new reaction to ZnO nanoparticles. Chem. Lett. 33: 770-771.
6. Ganeev, R.A., G.S. Boltaev, R.I. Tugushev and T. Usmanov. 2010. Nanoparticle formation during laser ablation of metals at different pressures of surrounding noble gases. Appl. Phys. 100: 119-123.
7. Hett, A. 2004. Nanotechnology: Small matters many unknown. Swiss Re, risk perception series, Zurich. pp. 275-282.
8. Kato, H. 2011. In vitro assays: Tracking nanoparticles inside cells. Nat. Nanotechnol. 6: 139-140.
9. Kawano, T. and H. Imai. 2006. Fabrication of ZnO nanoparticles with various aspect ratios through acidic and basic routes. Crystal Growth Desig. 6: 1054-1056.
10. Khorsand, Z., A. Ebrahimizadeh, M. Abrishami, A. Majid, W.H.R. Yousefi and S.M. Hosseini. 2011. Effect of annealing temperatrure on some structural and optical properties of ZnO nanoparticles prepared by a modified sol-gel combustion method. Ceram. Internat. 37: 393-398.
11. Kohler, M. and W. Fritzsche. 2008. Nanotechnology. John Wiley & Sons.
12. Kumar, B., K. Smita, L. Cumbal and A. Debut, 2014. Green approach for fabrication and applications of zinc oxide nanoparticles. Bioinorg. Chem. Appl. 7: 214-221.
13. Larson, D., W.R. Zipfel, R.M. Williams, S.W. Clark, M.P. Bruches and F.W. Wise. 2003. Watter soluble quantum dots for multi photon fluriscence imaging in vivo. Science 300: 1434-1436.
14. Lee, S., S. Jeong, D. Kim, S. Hwang, M. Jeon and J. Moon. 2008. ZnO nanoparticles with controlled shapes and sizes prepared using a simple polyol synthesis. Superlattices Microstru. 43: 330-339.
15. Lin, K.F., H.M. Cheng, H.C. Hsu, L.J. Lin and W.F. Hsieh, 2005. Band gap variation of size-controlled ZnO quantum dots synthesized by sol–gel method. Chem. Phys. Lett. 409: 208-211.
16. Nalwa, H.S. 1999. Handbook of nanostructured materials and nanotechnology, five-volume set. Academic Press. pp. 259.
17. Prasad, T., P. Sudhakar, Y. Sreenivasulu, P. Latha, V. Munaswamy, K.R. Reddy, T. Sreeprasad, P. Sajanlal and T. Pradeep. 2012. Effect of nanoscale zinc oxide particles on the germination, growth and yield of peanut. J. Plant Nutr. 35: 905-927.
18. Purica, M., E. Budianu and E. Rusu. 2001. ZnO thin films on semiconductor substrate for large area photodetector applications. Thin Solid Films 383: 284-286.
19. Razzaq, A., R. Ammara, H. Jhanzab, T. Mahmood, A. Hafeez and S. Hussain. 2015. A novel nanomaterial to enhance growth and yield of wheat. J. Nanosci. Technol. 45: 55-58.
20. Reddy, A.J., M.K. Kokila, H. Nagabhushana, S.C. Sharma, J.L. Rao, C. Shivakumara and R.P.S. Chakradhar. 2012. Structural, EPR, photo and thermo-luminescence properties of ZnO: Fe nanoparticles. Mater. Chem. Phys. 133: 876-883.
21. Rycenga, M., C.M. Cobley, J. Zeng, W. Li, C.H. Moran, Q. Zhang and Y. Xia. 2011. Controlling the synthesis and assembly of silver nanostructures for plasmonic applications. Chem. Rev. 111: 3669-3712.
22. Sabir, S., M. Arshad and S.K. Chaudhari, 2014. Zinc oxide nanoparticles for revolutionizing agriculture: Synthesis and applications. Sci. World J. 20: 1334-1342.
23. Saravanan, P., R. Gopalan and V. Chandrasekaran. 2008. Synthesis and characterisation of nanomaterials. Defen. Sci. J. 58: 504-510.
24. Sattler, K.D. 2010. Handbook of nanophysics: Principles and methods. CRC press.
25. Shevchenko, E.V., D.V. Talapin, N.A. Kotov, S. O'Brien and B. Christopher. 2006. Murray. Structural diversity in binary nanoparticle superlattices. Nature 439: 55-59.
26. Teja, A.S. and P.Y. Koh. 2009. Synthesis, properties, and applications of magnetic iron oxide nanoparticles. Prog. Crystal Growth Charact. Mater. 55: 22-45.
27. Uthirakumar, P., B. Karunagaran, N. Subramaniyam and C. H. Hong. 2007. Nanocrystalline ZnO particles: Low-temperature solution approach from a single

molecular precursor. J. Crystal Growth 304: 150–157.
28. Wang, H., C. Xie and D. Zeng, 2005. Controlled growth of ZnO by adding H_2O. J. Crystal Growth 277: 372-377.
29. Wang, Z.L. and W. Wu. 2012. Nanotechnology-enabled energy harvesting for self-powered micro-/nanosystems. Angewandte Chemie International Edition 51: 11700-11721.
.
30. Wang, Z.L., 2004. Zinc oxide nanostructures: Growth, properties and applications. Journal of Physics: Condensed Matt. 16: 829-835.
31. Yattinahalli, S., S. Kapatkar, N. Ayachit and S. Mathad, 2013. Synthesis and structural characterization of nanosized nickel ferrite. Int. J. Self-Propag. High-Temp. Syn. 22: 147-150

